



# Degradation and mineralization mechanism of phenol by BiPO<sub>4</sub> photocatalysis assisted with H<sub>2</sub>O<sub>2</sub>

Yanfang Liu, Yanyan Zhu, Jing Xu, Xiaojuan Bai, Ruilong Zong, Yongfa Zhu\*

Department of Chemistry, Beijing Key Laboratory for Analytical Methods and Instrumentation, Tsinghua University, Beijing 100084, China

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## ABSTRACT

Degradation and mineralization of phenol by BiPO<sub>4</sub> photocatalysis assisted with H<sub>2</sub>O<sub>2</sub> were attempted in order to know the effects of H<sub>2</sub>O<sub>2</sub> on BiPO<sub>4</sub> photocatalysis and the detailed mechanism. Both conversion and mineralization rate of phenol by BiPO<sub>4</sub> photocatalysis could be accelerated obviously by addition of H<sub>2</sub>O<sub>2</sub> above 30 ppm, whereas low concentration of H<sub>2</sub>O<sub>2</sub> could inhibit the mineralization rate of phenol due to the consumption of photogenerated holes (h<sup>+</sup>) by the adsorbed H<sub>2</sub>O<sub>2</sub> on BiPO<sub>4</sub>. The enhancement of efficiency by adequate H<sub>2</sub>O<sub>2</sub> resulted from the •OH produced by H<sub>2</sub>O<sub>2</sub> photolysis and the increased separation efficiency of e<sup>-</sup> and h<sup>+</sup> by the capture of e<sup>-</sup> by H<sub>2</sub>O<sub>2</sub>. •OH was efficient in conversion of phenol to its intermediates but it could not transfer the carboxylic ones without C–H bond into CO<sub>2</sub> and could induce the formation of dimeric intermediates. Therefore, phenol could not be completely mineralized by H<sub>2</sub>O<sub>2</sub>. In contrast to H<sub>2</sub>O<sub>2</sub> photolysis, the main active species of BiPO<sub>4</sub> photocatalysis were photogenerated holes, which were efficient in fast ring cleavage and mineralization of carboxylic intermediates. This resulted in the complete mineralization of phenol by BiPO<sub>4</sub> in 4 h. Synergy of BiPO<sub>4</sub> and adequate H<sub>2</sub>O<sub>2</sub> could raise the removal efficiency of phenol greatly.

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## 1. Introduction

BiPO<sub>4</sub>, a new efficient photocatalyst, shows more attractive activity than TiO<sub>2</sub> (P25, Degussa) [1,2]. The activity of BiPO<sub>4</sub> can be improved greatly by decreasing the particle size or hybridizing with carbon and C<sub>3</sub>N<sub>4</sub> [3–5]. Hybridization of C<sub>3</sub>N<sub>4</sub> on the surface of BiPO<sub>4</sub> can not only significantly improve UV light photocatalytic activity, but also induce dramatic visible light activity. Therefore, BiPO<sub>4</sub> is a promising photocatalyst and has much potential in remediation of environment.

Many organic pollutants can be degraded via hydroxyl radicals by H<sub>2</sub>O<sub>2</sub> under UV irradiation [6,7]. It was found that H<sub>2</sub>O<sub>2</sub> could significantly enhance the photocatalytic degradation of methylene blue by BiPO<sub>4</sub> photocatalyst [1], but the mechanism was not elucidated. The elucidation of degradation mechanism of organic pollutants is beneficial to select an appropriate and cost-effective remediation strategy to deal with water pollution. Phenol is highly toxic and very difficult to be degraded [8]. In addition, during the oxidation of phenol, hydroquinone (HQ) and benzoquinone (p-BQ) are formed, whose toxicities are several orders of magnitude higher than that of phenol itself [9]. Thus, it is necessary to clarify the

degradation and mineralization pathway of phenol in BiPO<sub>4</sub>–H<sub>2</sub>O<sub>2</sub> system.

This work attempts to elucidate the degradation mechanism of phenol by BiPO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> under UV irradiation. The effects of H<sub>2</sub>O<sub>2</sub> on the degradation and mineralization rate of phenol by BiPO<sub>4</sub> photocatalysis were obtained. The intermediates formed in the degradation process of phenol and the active species to degrade phenol were identified. Finally, the degradation mechanism of phenol by BiPO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> was proposed.

## 2. Experimental

### 2.1. Preparation and characterization of BiPO<sub>4</sub> photocatalyst

BiPO<sub>4</sub> was synthesized through a hydrothermal process [2]. All chemicals used were analytic grade reagents. In a typical procedure, 3 mmol of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and 120 mL distilled water were put into a beaker under magnetic stirring. Then 10.8 mmol of NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O was added into the mixture and stirred for 1 h. The resulting suspension was transferred into a Teflon-lined stainless steel autoclave and maintained at 160 °C for 24 h. The products were washed three times with distilled water and dried at 120 °C for 12 h. The morphology and structure of BiPO<sub>4</sub> samples before and after photocatalysis were examined with transmission electron microscopy (TEM), scanning electron microscope (SEM) and powder X-ray diffraction (XRD). The Brunauer Emmett Teller

\* Corresponding author. Tel.: +86 10 62787601; fax: +86 10 62787601.

E-mail address: [zhuyf@tsinghua.edu.cn](mailto:zhuyf@tsinghua.edu.cn) (Y. Zhu).

(BET) specific surface area and the pore size distribution of  $\text{BiPO}_4$  sample were characterized by nitrogen adsorption at 77 K with Micromeritics 3020.

## 2.2. Degradation experiments

Photocatalysis and photolysis experiments were performed under UV irradiation of an 11 W low pressure lamp ( $\lambda = 254 \text{ nm}$ ). The average light intensity was  $0.9 \text{ mW cm}^{-2}$  (measured with a power meter from the Institute of Electric Light Source). As for photocatalysis, 50 mg  $\text{BiPO}_4$  was added into 100 mL phenol solution ( $50 \text{ mg L}^{-1}$ ). Before the light was turned on, the solution was ultrasonicated for 10 min and then stirred for 30 min to ensure adsorption–desorption equilibrium of phenol on the catalysts. 3 mL of the solution was taken at given time intervals and separated through centrifugation (12,000 rpm, 10 min). Certain concentration of  $\text{H}_2\text{O}_2$  was added into the system before light was turned on. The active species to degrade phenol were detected through trapping by tert-butyl alcohol (t-BuOH) and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na). To confirm the main active species, electron spin resonance (ESR) was also conducted. ESR signals of radicals trapped by DMPO were recorded on a JEOL JES FA-200 spectrometer at ambient temperature under photoirradiation of 254 nm. Typical spectrometer parameters were as follows: center field 323.252 mT, sweep width 5 mT, microwave frequency 9.054 GHz, modulation frequency 100 kHz, power 2 mW. In order to quantitatively compare the concentration of hydroxyl radical under different conditions, the amount of solution sucked in the quartz capillary tube and the photoirradiation time were the same for all ESR measurements. Other conditions were as follows: the photocatalyst dosage, 0.5 g/L; and DMPO concentration, 0.03 mol/L.

## 2.3. Chemical analysis

The concentrations of phenol and most of its reaction intermediates were measured by HPLC (Lumtech) system. Venusil XBP-C<sub>18</sub> ( $250 \times 4.6 \text{ mm i. d.}$ ,  $5 \mu\text{m}$ ) reversed phase column was used. The mobile phase was a mixture of methanol and water (60:40, v/v) with a flow rate of  $1.0 \text{ mL min}^{-1}$ . The UV detector was operated at 270 nm. Further intermediate analysis was determined by HPLC-MS. The HPLC-MS spectrum was obtained using LC-MS (Thermo Fisher LTQ) equipped with an electrospray ionization source (ESI). The scan range was  $m/z$  50–500 in both negative and positive ion mode. HPLC series is equipped with a reversed-phase C<sub>18</sub> column. The mobile phase used for HPLC experiments was a mixture of methanol and water (60:40, v/v) with a flow rate of  $0.8 \text{ mL min}^{-1}$ . TOC was monitored with a Multi N/C 2100S TOC/TN analyzer. The samples were filtrated with  $0.45 \mu\text{m}$  millipore filter to remove any particles prior to injecting into HPLC and TOC analyzer.

## 3. Results and discussion

### 3.1. Degradation and mineralization kinetics of phenol

As observed in Fig. 1, the control experiments were performed under different conditions. Phenol could be degraded by both  $\text{BiPO}_4$  and  $\text{H}_2\text{O}_2$ . The degradation process followed pseudo-first-order kinetics model. As can be seen, when  $\text{H}_2\text{O}_2$  was added into  $\text{BiPO}_4$ –phenol system, the apparent rate constant  $k$  increased as  $C(\text{H}_2\text{O}_2)$  increased, indicating that  $\text{H}_2\text{O}_2$  was favorable for the degradation of phenol by  $\text{BiPO}_4$ . However,  $k$  (60 ppm  $\text{H}_2\text{O}_2$  +  $\text{BiPO}_4$ ) was smaller than  $k$  (60 ppm  $\text{H}_2\text{O}_2$ ), suggesting an inhibition of  $\text{BiPO}_4$  on  $\text{H}_2\text{O}_2$  in the degradation process of phenol.

TOC was conducted to elucidate the effects of  $\text{H}_2\text{O}_2$  on the mineralization rate of phenol by  $\text{BiPO}_4$  photocatalysis. About 40% TOC was removed by  $\text{BiPO}_4$  but less than 10% was removed by 60 ppm

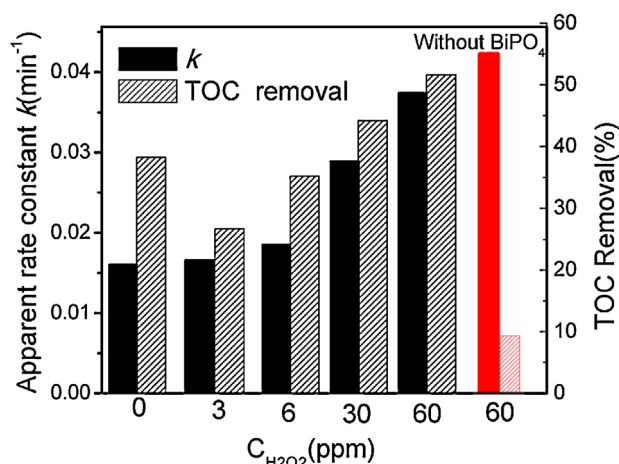


Fig. 1. Apparent rate constant and TOC removal percentage (after reacted for 2 h) at different concentrations of  $\text{H}_2\text{O}_2$  (Black color represents with  $\text{BiPO}_4$  and red color represents without  $\text{BiPO}_4$ ). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

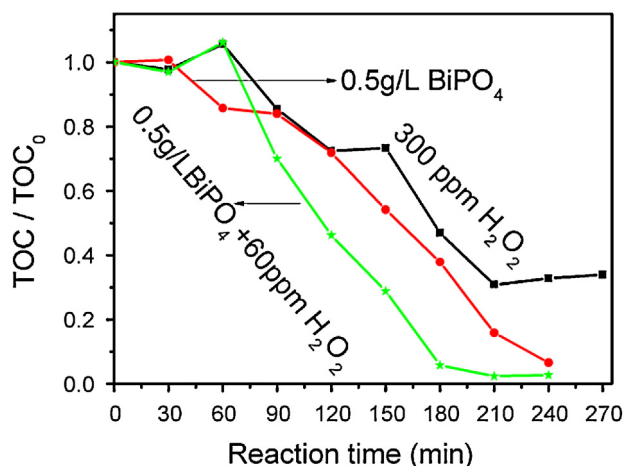


Fig. 2. Change of TOC in the degradation process of phenol by photocatalysis and 300 ppm  $\text{H}_2\text{O}_2$ .

$\text{H}_2\text{O}_2$  after reacted for 2 h. This meant that  $\text{BiPO}_4$  was superior to  $\text{H}_2\text{O}_2$  in mineralizing phenol. TOC was removed by 52% when 60 ppm  $\text{H}_2\text{O}_2$  was added into  $\text{BiPO}_4$ –phenol system, indicating a synergic effect between  $\text{BiPO}_4$  and  $\text{H}_2\text{O}_2$ . However, reduction of TOC with  $\text{BiPO}_4$  photocatalysis was inhibited by  $\text{H}_2\text{O}_2$  below 30 ppm. Based on the value of  $k$  and TOC removal percentage, it was concluded that  $\text{H}_2\text{O}_2$  was efficient in degrading phenol but inferior in deep mineralization. To confirm this proposition, 300 ppm  $\text{H}_2\text{O}_2$  (about 16 times the stoichiometric amount for complete mineralization of phenol [10]) was used to degrade phenol. HPLC result (Supporting Information Fig. S1) showed that phenol was completely converted into intermediates in 60 min and all intermediates could be degraded in 210 min. However, only 70% TOC was removed (Fig. 2). These results implied that phenol could not be completely mineralized by  $\text{H}_2\text{O}_2$ . However, phenol could be completely mineralized by  $\text{BiPO}_4$  in 4 h, confirming its strong ability for the deep mineralization of phenol.

As reported before, with the BET surface area of  $\text{BiPO}_4$  being  $3.7 \text{ m}^2/\text{g}$  (the Nitrogen adsorption desorption isotherms and the pore size distribution curve of  $\text{BiPO}_4$  have been provided in the Supporting Information Fig. S2), the adsorption of phenol on  $\text{BiPO}_4$  was negligible, with only less than 3% phenol adsorbed on  $\text{BiPO}_4$  (Supporting Information Fig. S3). So adsorption is not the reason

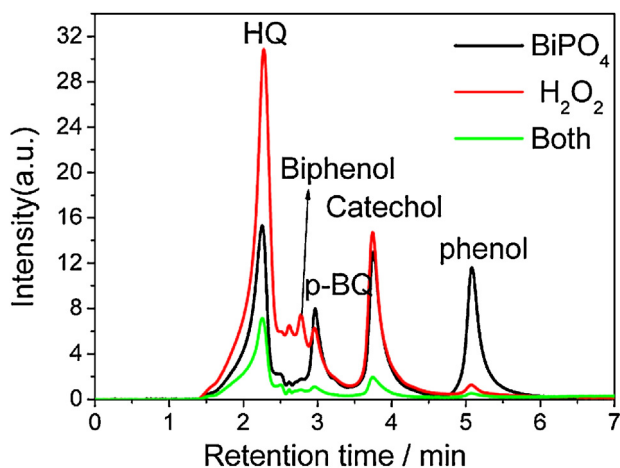


Fig. 3. HPLC spectrums of phenol solution degraded by BiPO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> separately and simultaneously under UV irradiation.

for the efficient degradation of phenol by BiPO<sub>4</sub>. The high activity of BiPO<sub>4</sub> owes to the high potential of photogenerated holes in the valence band as well as the high separation efficiency of electron hole pairs, which has been discussed in detail in our previous work [1]. To test the stability of the samples during the photocatalytic process, the morphology and structure of BiPO<sub>4</sub> samples before and after photocatalysis were examined with TEM, SEM and XRD (Supporting Information Figs. S4–S6). After reaction, no obvious change has been observed, indicating its good stability. This has also been reported in our previous work [1]. From Fig. 2, it could be seen that 60 ppm H<sub>2</sub>O<sub>2</sub> could accelerate the mineralization rate with BiPO<sub>4</sub> photocatalyst.

### 3.2. Analysis of degradation intermediates

Samples for HPLC analysis were taken after reacted for 120 min. Fig. 3 showed that there were three common intermediates under the three kinds of degradation conditions (BiPO<sub>4</sub>/UV, H<sub>2</sub>O<sub>2</sub>/UV and BiPO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>/UV). In H<sub>2</sub>O<sub>2</sub>/UV system, two minor intermediates formed, which were not detected in BiPO<sub>4</sub>/UV and BiPO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>/UV system. The intermediates were further identified by HPLC-MS (Supporting Information Fig. S7). The intermediate at *m/z* 181 in the negative model and *m/z* 205 in the positive model could be definitely identified as dimeric intermediate of phenol. Based on the retention time, this intermediate corresponds to the minor intermediate detected by HPLC in H<sub>2</sub>O<sub>2</sub>/UV system, which was not detected in BiPO<sub>4</sub>/UV system by HPLC. The *m/z* values had some deviation from the molecular weight of the dimeric intermediate (186) due to the loss of hydrogen or addition of H<sub>3</sub>O<sup>+</sup>. There were five possible structures of dimeric intermediates. The formation mechanism of these dimeric intermediates was illustrated in Scheme 1. Based on steric effect, 4-phenoxyphenol and 4, 4'-dihydroxybiphenyl were easier to form. It was reported that the coupling of free phenoxy radicals under acidic conditions would favor the C–C coupling, whereas C–O coupling mainly occurred under basic conditions [11,12]. In this work, an acidic condition pH (5.8) favored C–C coupling, hence 4, 4'-dihydroxybiphenyl should be the main intermediate. This intermediate was also reported by previous studies [12–14]. The common intermediates in the HPLC chromatograms could be confirmed as HQ, p-BQ and catechol [15–18], and the elution order was HQ, p-BQ and catechol [19]. These aromatic intermediates were in much larger amount in H<sub>2</sub>O<sub>2</sub>–phenol system compared with that in BiPO<sub>4</sub>–phenol system. And the TOC removal rate in H<sub>2</sub>O<sub>2</sub>–phenol system was much smaller than that in BiPO<sub>4</sub>–phenol system (Fig. 4). These results

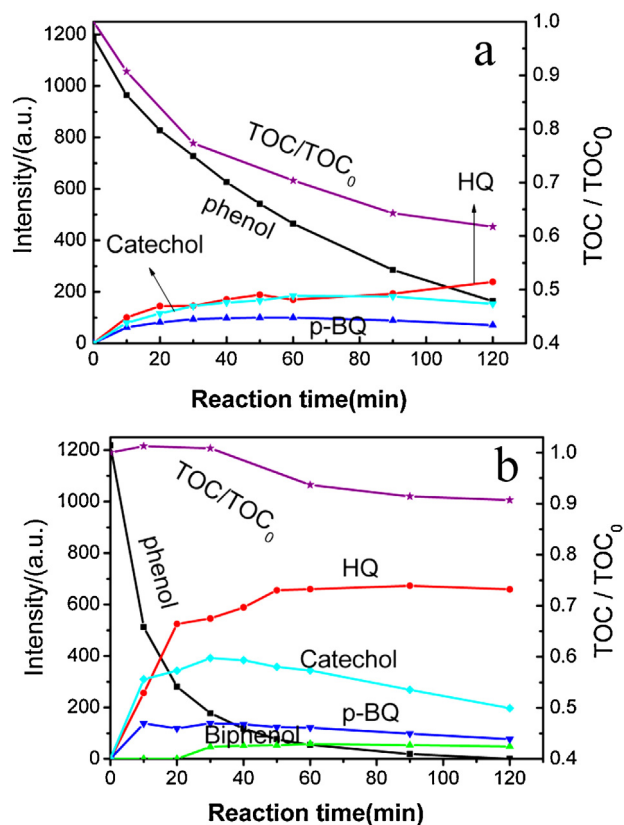
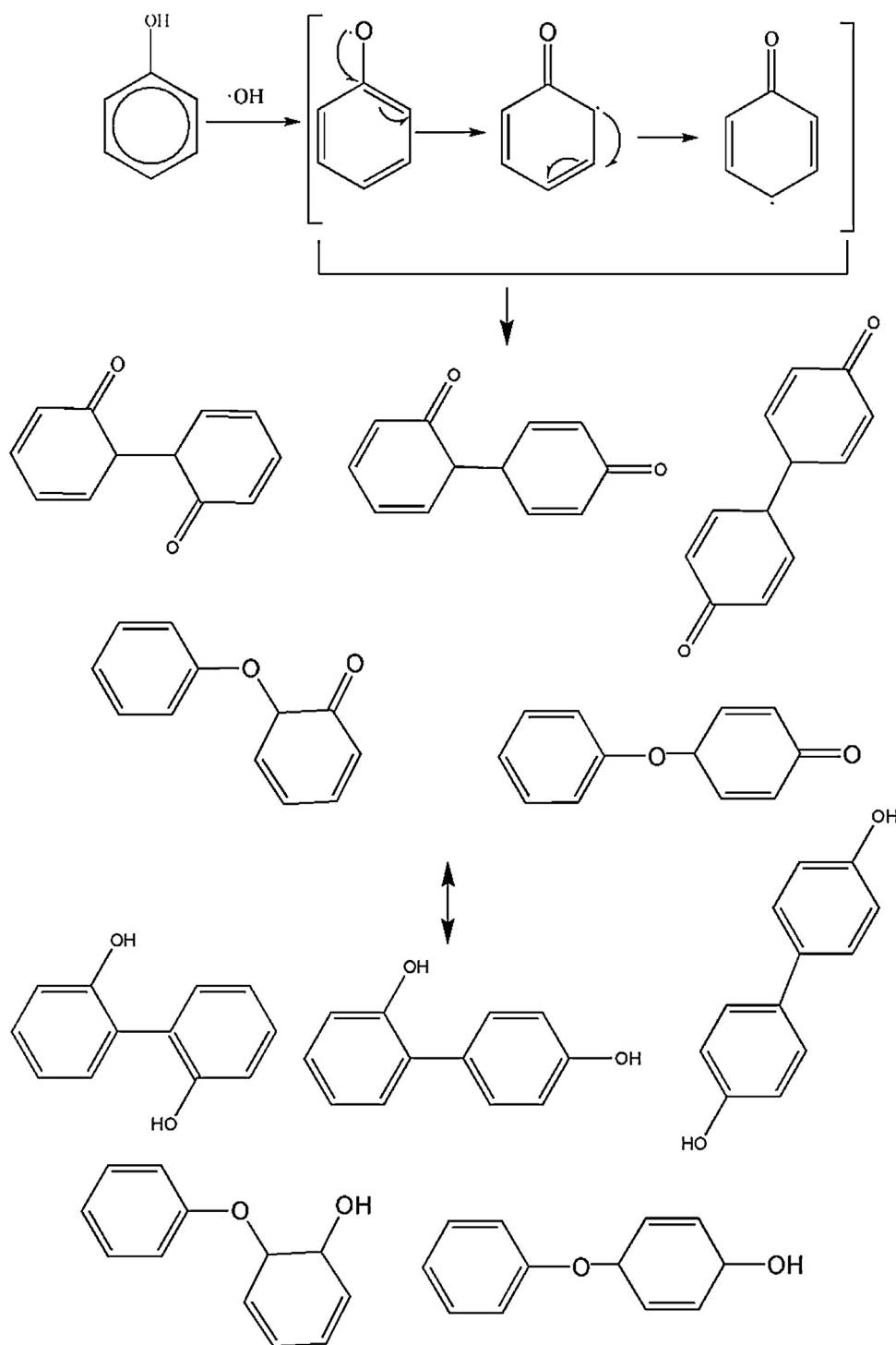


Fig. 4. Distribution of the intermediates and the change of TOC in the degradation process of phenol by BiPO<sub>4</sub> (a) and H<sub>2</sub>O<sub>2</sub> (b) under UV irradiation.

confirmed our proposition that H<sub>2</sub>O<sub>2</sub> was efficient in conversion of phenol but inferior in deep mineralization compared with BiPO<sub>4</sub> photocatalysis. Carboxylic acids were reported to be the ring-opened intermediates of phenol [20], but they were not detected. This may be due to their low concentration and the inappropriate detection wavelength for carboxylic acids, making them unable to be detected by LC and LC-MS.

### 3.3. Identification of the active species

The radicals and holes trapping experiments as well as the ESR experiments were designed to identify the main active species. EDTA-2Na was used as hole scavenger and t-BuOH as hydroxyl radical scavenger [21]. As shown in Fig. 5a, the photodegradation rate of phenol with BiPO<sub>4</sub> was slightly suppressed by the addition of hydroxyl radical scavenger, while it was obviously inhibited by hole scavenger. This indicated that photogenerated holes were the main active species in BiPO<sub>4</sub> photocatalysis. This was consistent with the oxidation of phenol by iodine-doped titanium dioxide [22] and degradation of organic pollutants by Bi<sub>2</sub>WO<sub>6</sub> photocatalysis [23,24]. However, it seemed to be contradictory with the previous report that hydroxyl radicals were the main active species in degradation of methylene blue (MB) by BiPO<sub>4</sub> [1]. This may be due to the different characteristics of MB and phenol since the main active species not only depends on the type of photocatalyst, but also on the characteristics of the organic compounds to be degraded [25]. MB may not interact with the photogenerated hole directly because of its cationic nature and its degradation is initiated by •OH via the abstraction of hydrogen from C–H bonds [26]. Thus hydroxyl radicals are more likely to be the main active species in degradation of MB by BiPO<sub>4</sub>. However, with an anionic nature and fewer C–H bonds, phenol may be much easier to be degraded via



**Scheme 1.** The formation mechanism of the dimeric intermediates in the degradation of phenol.

electron transfer with photogenerated holes than attacked by hydroxyl radicals. In addition, some degradation intermediates of phenol with electron-donating groups are much easier to be degraded via electron transfer. The pH of phenol solution was lower than MB solution. This acidic condition was not favorable for the oxidation of  $\text{OH}^-$  by  $h^+$  (Eq. (1))



Thus photogenerated holes are the predominant oxidant for the degradation of phenol by  $\text{BiPO}_4$  photocatalysis. It should be noted

that 4,4'-dihydroxybiphenyl was detected by HPLC when photo-generated holes were scavenged by EDTA-2Na in the photocatalysis system. This dimeric intermediate was also detected in  $\text{H}_2\text{O}_2/\text{UV}$  system as mentioned above. Therefore, it was supposed that 4,4'-dihydroxybiphenyl was easier to form when  $\cdot\text{OH}$  was the main active species. Fig. 5b showed that t-BuOH significantly suppressed the degradation rate of phenol by  $\text{H}_2\text{O}_2/\text{UV}$ , whereas EDTA-2Na hardly affected it. This indicated that hydroxyl radicals were the active species in  $\text{H}_2\text{O}_2/\text{UV}$  system. To confirm these conclusions, we measured  $\cdot\text{OH}$  radicals formed in the presence of  $\text{BiPO}_4$  or  $\text{H}_2\text{O}_2$



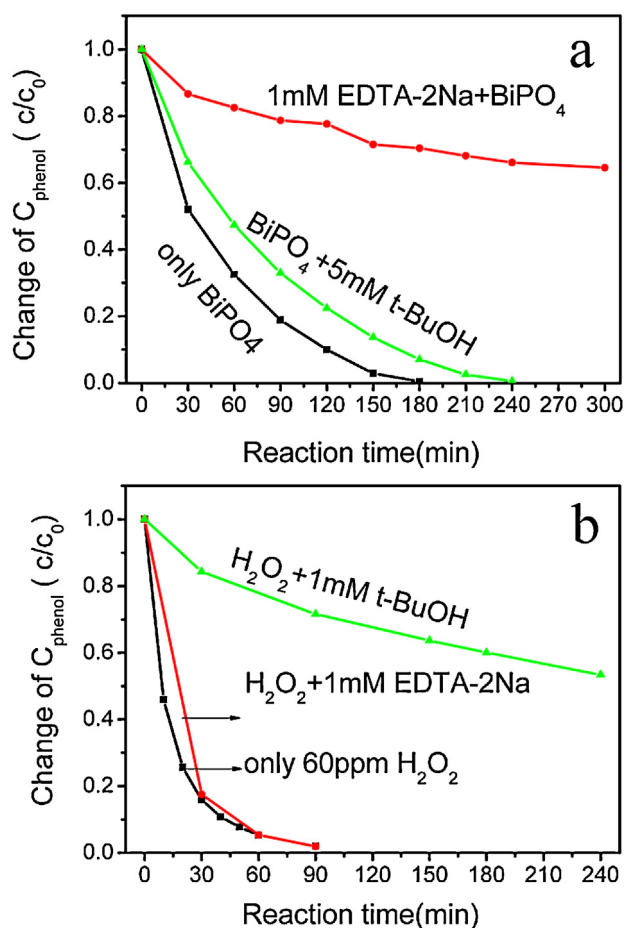


Fig. 5. Trapping experiments for phenol degradation by  $\text{BiPO}_4$  (a), and  $\text{H}_2\text{O}_2$  (b) under UV light irradiation.

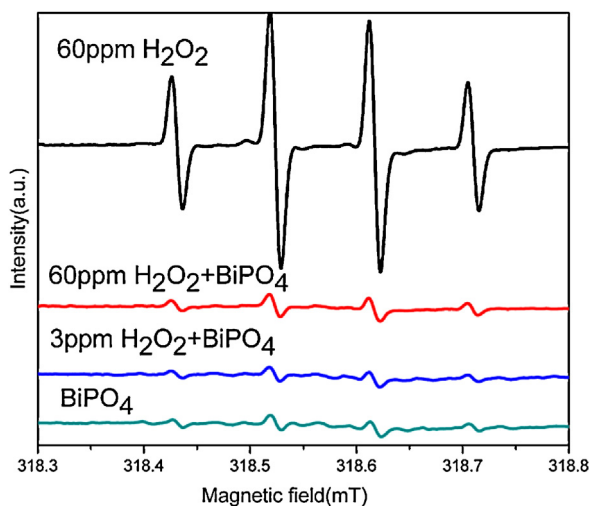
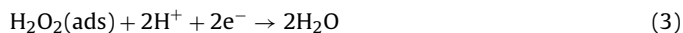


Fig. 6. DMPO spin-trapping ESR spectra under UV irradiation for 4 min at room temperature of water in the presence of  $\text{BiPO}_4$ ,  $\text{H}_2\text{O}_2$  or both  $\text{BiPO}_4$  and  $\text{H}_2\text{O}_2$ .

by ESR using DMPO as the spin-trap reagent. As shown in Fig. 6, the characteristic four peaks of DMPO- $\cdot\text{OH}$  with intensity 1:2:2:1 appeared in all spectra. The intensity of  $\cdot\text{OH}$  generated in  $\text{BiPO}_4$  suspension was much lower than that in  $\text{H}_2\text{O}_2$  system, which indicated that the photogenerated holes in the valence band of  $\text{BiPO}_4$  reacted slowly with surface-bound water or hydroxyl group, producing small amount of  $\cdot\text{OH}$ . Addition of 3 ppm  $\text{H}_2\text{O}_2$  hardly increased

the amount of  $\cdot\text{OH}$  formed in  $\text{BiPO}_4$  suspension, whereas 60 ppm  $\text{H}_2\text{O}_2$  could increase it. However, the  $\cdot\text{OH}$  formed in  $\text{BiPO}_4$ - $\text{H}_2\text{O}_2$  (60 ppm) system was much less than that in  $\text{H}_2\text{O}_2$  (60 ppm) system. These results could be explained based on Auguliano's and Wang's research results [27,28] and the catalytic mechanism of  $\text{H}_2\text{O}_2$ .  $\text{H}_2\text{O}_2$  is prone to adsorb on the catalyst's surface and the adsorbed  $\text{H}_2\text{O}_2$  would react with holes or electrons on the catalyst's surface as the Eqs. (2) and (3) [27]:

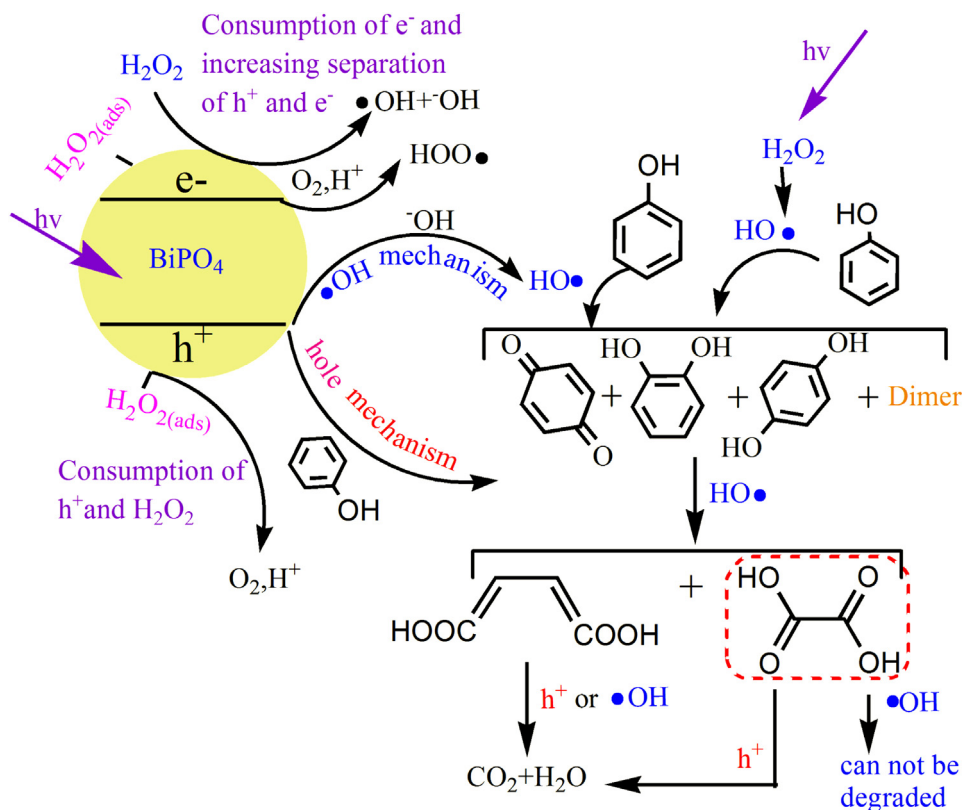


Since  $\text{H}_2\text{O}_2$  was consumed in the two reactions, the formation of  $\cdot\text{OH}$  was reduced in  $\text{BiPO}_4$ - $\text{H}_2\text{O}_2$  system. Meanwhile, since the holes governed the mineralization rate of phenol by  $\text{BiPO}_4$ , consumption of holes by adsorbed  $\text{H}_2\text{O}_2$  would result in retarded photocatalytic mineralization of phenol. This is why reduction of TOC with  $\text{BiPO}_4$  photocatalysis was inhibited by  $\text{H}_2\text{O}_2$  below 30 ppm. When saturated adsorption of  $\text{H}_2\text{O}_2$  on  $\text{BiPO}_4$  was achieved and the amount of free  $\text{H}_2\text{O}_2$  increased, lots of  $\cdot\text{OH}$  radicals were produced by  $\text{H}_2\text{O}_2$  photolysis. This would accelerate the conversion rate of phenol. Besides, as electron scavenger,  $\text{H}_2\text{O}_2$  could react with electrons as Eq. (4) [29]. This would increase the separation efficiency of photogenerated electrons and holes. So, both the conversion and mineralization rate of phenol were accelerated with adequate  $\text{H}_2\text{O}_2$ .



### 3.4. Degradation mechanism of phenol

As described above, the main active species that oxidizes phenol by  $\text{BiPO}_4$  photocatalyst were photogenerated holes, which could lead to the fast cleavage of aromatic ring and were able to degrade the carboxylic acids formed in the degradation process of phenol [24]. By comparison,  $\cdot\text{OH}$  was superior in the conversion but inferior in the mineralization of phenol. This conclusion may be contradictory to the common belief that  $\cdot\text{OH}$  is the most powerful oxidant following fluorine. It can be explained by the way  $\cdot\text{OH}$  oxidizes organic molecules.  $\cdot\text{OH}$  tends to abstract hydrogen from C-H bond or add to unsaturated carbon-carbon bonds, so if a compound (such as oxalic acid, which is one of the intermediates in the degradation of phenol [20]) lacks abstractable hydrogen and unsaturated carbon-carbon bonds, then it cannot be degraded by  $\cdot\text{OH}$ . Sun and Pignatello [30] also found that radical mechanism predominated for 2,4-dichlorophenol transformation, whereas hole mechanism predominated for carboxyl-bearing byproducts formed during late stages of mineralization. Based on above analysis and literature [24,27,31], possible mechanisms of the two paths are proposed as follows. As illustrated in Scheme 2, phenol is degraded by  $\text{BiPO}_4$  mainly via hole direct oxidation mechanism. The holes generated by photocatalysis can oxidize phenol directly to form the ring cleavage products, which are further mineralized into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  through photo-Kolbe reaction. Since radical mechanism could also take place, hydroxylated products were also detected in  $\text{BiPO}_4$ -phenol system, but they were in relatively minor amount compared with that in  $\text{H}_2\text{O}_2$ -phenol system (Fig. 4). Under UV irradiation,  $\text{H}_2\text{O}_2$  can produce hydroxyl radicals via photodecomposition [32], and degradation of phenol by  $\text{H}_2\text{O}_2$ /UV are through hydroxyl radical mechanism. In this process, large amounts of hydroxylated products form, and then they are degraded to carboxylic acids. Among these products, the ones without C-H bond and some difficult degradable carboxylic acids cannot be further mineralized into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . In addition, dimeric intermediates are easier to form when  $\cdot\text{OH}$  is the main active species. The formation pathway of dimeric intermediates is illustrated in Scheme 1.



**Scheme 2.** Degradation mechanism of phenol by BiPO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>.

In this process,  $\bullet\text{OH}$  abstracts hydrogen of the hydroxyl on phenol, forming phenoxy radicals. Since  $\bullet\text{OH}$  facilitates the formation of phenoxy radicals, which is the rate controlling step of oxidative coupling of phenols to form a dimer [33], dimeric intermediates are easier to form when  $\bullet\text{OH}$  is the main active species. When low concentration of H<sub>2</sub>O<sub>2</sub> is added to BiPO<sub>4</sub> photocatalysis system, the adsorbed H<sub>2</sub>O<sub>2</sub> on BiPO<sub>4</sub> photocatalyst's surface would react with holes and decrease the mineralization rate of phenol by BiPO<sub>4</sub>. Adequate H<sub>2</sub>O<sub>2</sub> can not only produce lots of  $\bullet\text{OH}$  radicals, but also increase the separation rate of  $e^-$  and  $h^+$  by scavenging electrons. Therefore, both the conversion and mineralization rate of phenol can be accelerated by adequate H<sub>2</sub>O<sub>2</sub>.

#### 4. Conclusion

Degradation and mineralization efficiency and mechanism of phenol by BiPO<sub>4</sub> photocatalyst assisted with H<sub>2</sub>O<sub>2</sub> were investigated. Both conversion and mineralization rate of phenol by BiPO<sub>4</sub> could be accelerated obviously by addition of H<sub>2</sub>O<sub>2</sub> above 30 ppm. The main active species of H<sub>2</sub>O<sub>2</sub> photolysis is  $\bullet\text{OH}$ . It is efficient in conversion of phenol to its aromatic intermediates but is not able to completely mineralize phenol. By comparison, the main active species of BiPO<sub>4</sub> photocatalysis are photogenerated holes. They are efficient in fast ring cleavage of phenol and mineralization of carboxylic intermediates. Synergy of BiPO<sub>4</sub> and adequate H<sub>2</sub>O<sub>2</sub> can raise the removal efficiency of phenol greatly through the production of large amount of  $\bullet\text{OH}$  and the increased separation efficiency of  $e^-$  and  $h^+$  by the capture of  $e^-$  by H<sub>2</sub>O<sub>2</sub>.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.05.049>.

#### References

- [1] C. Pan, Y. Zhu, *Environmental Science & Technology* 44 (2010) 5570–5574.
- [2] Y. Liu, X. Ma, X. Yi, Y. Zhu, *Acta Physico-Chimica Sinica* 28 (2012).
- [3] C. Pan, Y. Zhu, *Journal of Materials Chemistry* 21 (2011) 4235–4241.
- [4] B. Lu, X. Ma, C. Pan, Y. Zhu, *Applied Catalysis A-General* 435 (2012) 93–98.
- [5] C. Pan, J. Xu, Y. Wang, D. Li, Y. Zhu, *Advanced Functional Materials* 22 (2012) 1518–1524.
- [6] Y.P. Huang, J. Li, W.H. Ma, M.M. Cheng, J.C. Zhao, J.C. Yu, *Journal of Physical Chemistry B* 108 (2004) 7263–7270.
- [7] M.M. Cheng, W.H. Ma, J. Li, Y.P. Huang, J.C. Zhao, *Environmental Science & Technology* 38 (2004) 1569–1575.
- [8] B. Iurascu, I. Siminiceanu, D. Vione, M.A. Vicente, A. Gil, *Water Research* 43 (2009) 1313–1322.
- [9] A. Santos, P. Yustos, A. Quintanilla, F. Garcia-Ochoa, J.A. Casas, J.J. Rodriguez, *Environmental Science & Technology* 38 (2004) 133–138.
- [10] M.S. Yalfani, S. Contreras, F. Medina, J. Sueiras, *Applied Catalysis B-Environmental* 89 (2009) 519–526.
- [11] S. Kobayashi, H. Higashimura, *Progress in Polymer Science* 28 (2003) 1015–1048.
- [12] L. Liu, H. Liu, Y.-P. Zhao, Y. Wang, Y. Duan, G. Gao, M. Ge, W. Chen, *Environmental Science & Technology* 42 (2008) 2342–2348.
- [13] E.B. Azevedo, F.R.D. Neto, M. Dezotti, *Applied Catalysis B-Environmental* 54 (2004) 165–173.
- [14] J. Yu, K.E. Taylor, H.X. Zou, N. Biswas, J.K. Bewtra, *Environmental Science & Technology* 28 (1994) 2154–2160.
- [15] Z. Guo, R. Ma, G. Li, *Chemical Engineering Journal* 119 (2006) 55–59.
- [16] R. Klaewkla, S. Kulprathipanja, P. Rangsunvigit, T. Rirksomboon, L. Nemeth, *Chemical Communications* (2003) 1500–1501.

- [17] J.S. Choi, S.S. Yoon, S.H. Jang, W.S. Ahn, *Catalysis Today* 111 (2006) 280–287.
- [18] I.e.a. Fatimah, *Arabian Journal of Chemistry* 8 (2011).
- [19] J.Q. Qiao, N. Yuan, C.J. Tang, J. Yang, J. Zhou, H.Z. Lian, L. Dong, *Research on Chemical Intermediates* 38 (2012) 549–558.
- [20] J.A. Zazo, J.A. Casas, A.F. Mohedano, M.A. Gilarranz, J.J. Rodriguez, *Environmental Science & Technology* 39 (2005) 9295–9302.
- [21] Z. Hao, Z. Ruilong, Z. Jincai, Z. Yongfa, *Environmental Science & Technology* 42 (2008) 3803–3807.
- [22] Z. He, L. Xie, J. Tu, S. Song, W. Liu, Z. Liu, J. Fan, Q. Liu, J. Chen, *Journal of Physical Chemistry C* 114 (2010) 526–532.
- [23] H.B. Fu, C.S. Pan, W.Q. Yao, Y.F. Zhu, *Journal of Physical Chemistry B* 109 (2005) 22432–22439.
- [24] C. Wang, H. Zhang, F. Li, L. Zhu, *Environmental Science & Technology* 44 (2010) 6843–6848.
- [25] L. Yang, L.E. Yu, M.B. Ray, *Environmental Science & Technology* 43 (2009) 460–465.
- [26] Z. Yu, S.S.C. Chuang, *Journal of Physical Chemistry C* 111 (2007) 13813–13820.
- [27] V. Auguliaro, E. Davi, L. Palmisano, M. Schiavello, A. Sclafani, *Applied Catalysis* 65 (1990) 101–116.
- [28] C. Wang, L. Zhu, M. Wei, P. Chen, G. Shan, *Water Research* 46 (2012) 845–853.
- [29] E.S. Elmolla, M. Chaudhuri, *Desalination* 252 (2010) 46–52.
- [30] Y.F. Sun, J.J. Pignatello, *Environmental Science & Technology* 29 (1995) 2065–2072.
- [31] S.K. Pardeshi, A.B. Patil, *Solar Energy* 82 (2008) 700–705.
- [32] T.S. Natarajan, M. Thomas, K. Natarajan, H.C. Bajaj, R.J. Tayade, *Chemical Engineering Journal* 169 (2011) 126–134.
- [33] A.C.D. Pimenta, J.E. Kilduff, *Journal of Colloid and Interface Science* 293 (2006) 278–289.